

APPENDIX F

Development of COC Depletion Estimates from LNAPL Under Diffusion-Limited Conditions

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F-1.0 INTRODUCTION

Appendix F describes the data and methods employed to estimate the potential additional time needed to meet mass-flux goals for chemicals of concern (COCs) emanating from low-permeability affected soils in the off-site area under diffusion-limited conditions. These timeframes are in addition to those presented in Appendices D and E.

F-2.0 METHOD FOR ESTIMATING MASS FLUX UNDER DIFFUSION-LIMITED CONDITIONS

Diffusion-limited mass flux may occur from low-permeability, residual light nonaqueous phase liquid (LNAPL)-affected soils in the off-site area. Only diffusion in the aqueous phase is considered in this appendix. While vapor-phase diffusion may be important for some low-permeability affected soils in the vadose zone, especially when considering the timeframe over which pulse soil-vapor extraction (SVE) operations will be carried out, diffusion-limited mass flux from saturated soils in and below the capillary fringe are likely to result in the most limiting timeframes.

Under conditions of sufficiently low horizontal and vertical hydraulic gradient and/or low permeability, diffusion of COCs in the aqueous phase may become the limitation on mass flux reduction. Low permeability may be a result of low intrinsic soil permeability and/or low relative permeability due to significant pore space occupied by other stationary fluid phases (e.g., LNAPL). Diffusion from a semi-infinite, low-permeability material with an initial uniform contaminant concentration, c_o , and boundary condition of zero contaminant concentration at the interface between the low- and high-permeability materials is given by Bear et al. (1994) as:

$$j = c_o \phi \sqrt{\frac{D_i^*}{\pi t}} \quad \text{F.1}$$

Where:

J = mass flux per unit area [$\text{MT}^{-1}\text{L}^{-2}$]

ϕ = porosity [-]

D_i^* = effective diffusivity [L^2T^{-1}], and

t = time [T]

The concentration distribution within the low permeability material is given (Bear et al., 1994) as:

$$\frac{c(x, t)}{c_o} = \text{erf} \frac{x}{\sqrt{4D_i^* t}} \quad \text{F.2}$$

Where:

x = distance into the low-permeability material [L]

In order to account for diffusion under transient conditions, Bear et al. (1994) state that the diffusivity should be divided by a retardation factor. Rixey and Joshi (2002) suggest a retardation factor that accounts for retardation both by diffusion into and out of a NAPL and sorption onto soil solids:

$$R = 1 + \frac{S_o}{S_w} K_{o-w} + \frac{\rho_b}{\phi} K_d \quad \text{F.3}$$

Where:

S_o = oil saturation [-]

S_w = water saturation [-]

K_{o-w} = oil-water partition coefficient [-]

ρ_b = soil bulk density [ML⁻³], and

K_d = soil-water partition coefficient [L³M⁻¹]

In the case where significant LNAPL is present in the pore space and there are no significant sources of non-LNAPL organic carbon in the soil, the third term on the left side of Equation F.3 may be neglected. Including the retardation factor into Equation F.1 as recommended, replacing the mass flux per unit area, j [ML⁻²T⁻¹], with the total mass flux, J [MT⁻¹], divided by the total interface area of the low-permeability material, A [L²], calculating the initial concentration as the solubility limit, c_s [ML⁻³], times the mole (mass) fraction in the LNAPL, f_o [-], and solving for t gives:

$$t = \left(\frac{Ac_s f_o \phi}{J} \right)^2 \frac{D_i^*}{\pi \left(1 + \frac{S_o}{S_w} K_{o-w} \right)} \quad \text{F.4}$$

A similar modification of Equation F.2 with the retardation factor gives:

$$\frac{c(x,t)}{c_o} = \text{erf} \frac{x}{\sqrt{\frac{4D_i^* t}{\left(1 + \frac{S_o}{S_w} K_{o-w} \right)}}} \quad \text{F.5}$$

F-3.0 ESTIMATION OF MASS FLUX UNDER DIFFUSION-LIMITED CONDITIONS

Equation F.4 is used to evaluate the timeframe over which diffusion-limited COC mass flux from low-permeability soils will exceed the mass-flux limits of 5 grams per day (g/day) given in Appendix D. The fine-grained clayey silts discussed in Appendices B and C are assumed to present the greatest potential for diffusion-limited mass flux. The distribution of these clayey silts in the off-site area (Appendix C) extends across a horizontal area of 134,000 square feet (ft²), which is assumed to be the interfacial area, A . This assumption implies diffusion out of only the lower face of the clayey silts. The interface area may be larger than this estimate because of surface irregularities. The 97.5% upper confidence limit of the oil (NAPL) saturation in the clayey silt is estimated to be 0.023 (Appendix C). Water is assumed to fill the remaining pore space. Total porosity is given in Appendix B as 0.401.

Benzene and methyl tertiary-butyl ether (MTBE) are the considered COCs, but because benzene tends to be more readily degraded, MTBE is the chemical that will be assessed with regard to diffusion-limited mass flux. The mean and 97.5% upper confidence limit of mass fraction of MTBE in the LNAPL are 0.00211 and 0.00301, respectively (Appendix C). A smaller mass fraction of MTBE measured from site-specific samples of LNAPL is given in Appendix D as 0.0004. The aqueous solubility limit of MTBE is 42,000 milligrams per liter (mg/l) (European Fuel Oxygenates Association, 2002). Rixey and Joshi (2000) give an effective diffusion coefficient for MTBE of 0.00015 square feet per day (ft²/day) and a gasoline-water partition coefficient of 16 to 18.

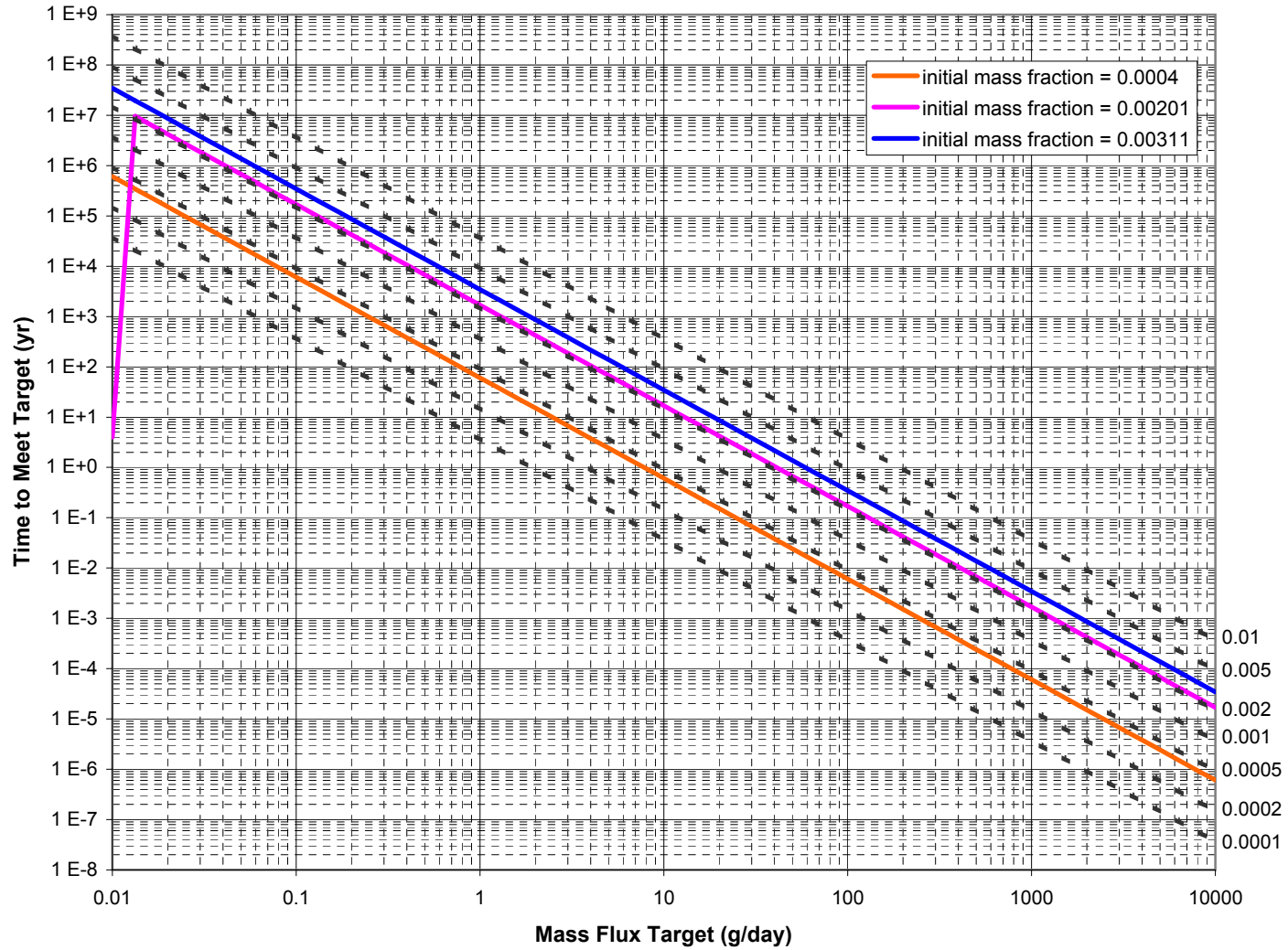
Using these values, the most conservative mass fraction of MTBE in LNAPL, Equation F.4 estimates about 140 years of diffusion-limited mass flux above the mass-flux target. The next lower mass fraction estimate results in about 70 years above the target, and the lowest mass fraction estimate results in about 3 years above the target. These results are shown graphically for a range of mass-flux targets in Figure F.1. Also shown on the figure are a family of lines for initial MTBE mass fractions from 0.0001 to 0.01, relating mass-flux targets to time for which mass flux is above the target.

The concentration profile predicted by Equation F.5 is shown on Figure F.2 as each of the site-specific MTBE mass fractions. Also shown on the figure is a family of lines for initial MTBE mass fractions from 0.0001 to 0.01 showing the concentration profile in the low-permeability material. The assumptions that the low-permeability material is uniformly contaminated to an equilibrium concentration and is infinitely thick conservatively increase the estimated timeframes. These curves suggest that for the approximate actual thickness of 3 feet for the low-permeability soils, the diffusion-limited mass flux may be over-predicted at late times for initial MTBE mass fractions above 0.001.

F-4.0 REFERENCES

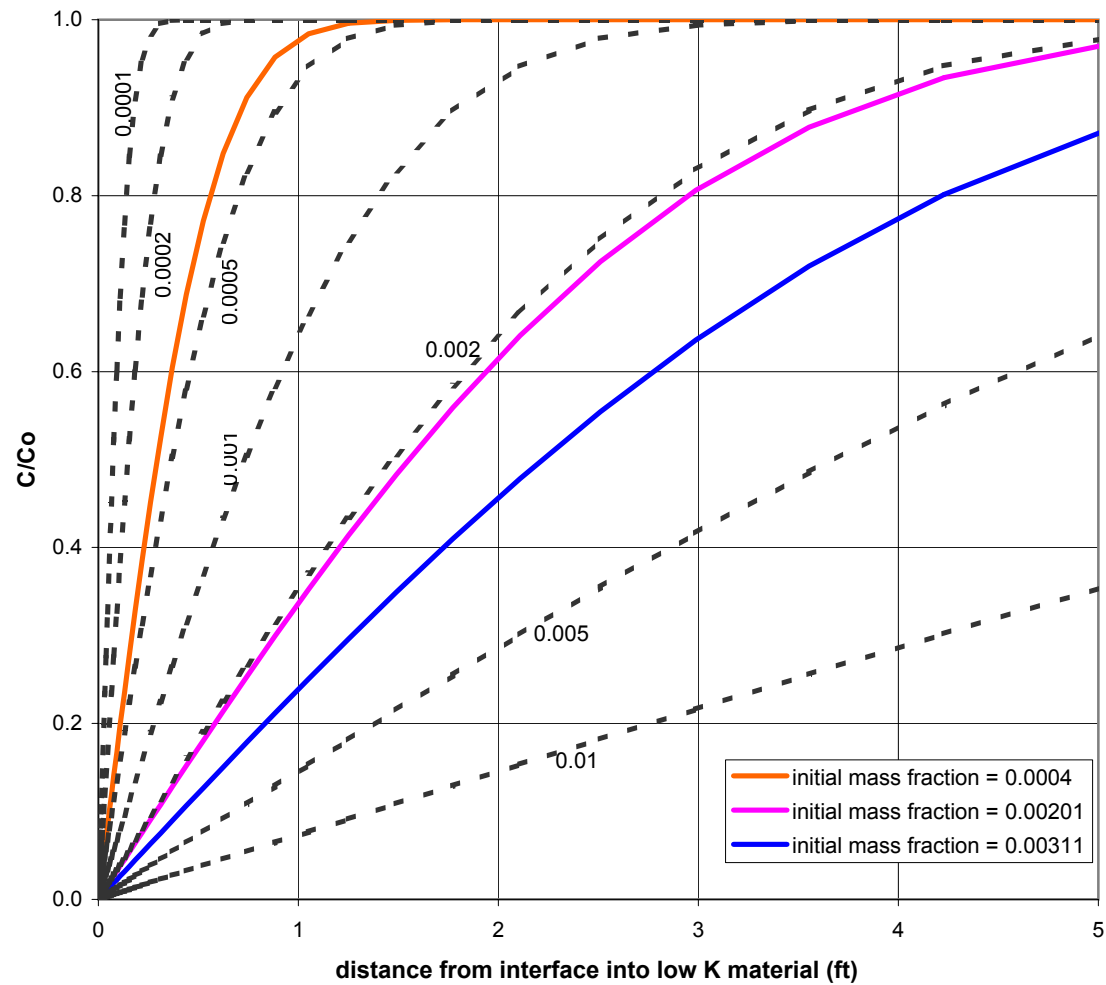
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- Rixey, W.G., and S. Joshi. 2000. Dissolution of MTBE from a Residually Trapped Gasoline Source. American Petroleum Institute. September.
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Figure F-1
Time Required to Meet Mass Flux Targets under Diffusion Limited Conditions
 Mission Valley Terminal, San Diego, California



*Dashed lines shown for several values of initial MTBE mass fraction indicated at right side of graph.

Figure F-2
MTBE Concentration Profile within Low Permeability Material at Target Flux of 5 g/day
Mission Valley Terminal, San Diego, California



*Dashed curves shown for several values of initial MTBE mass fraction indicated adjacent to curve.